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A combinatorial characterization scheme for high-throughput investigations of hydrogen storage materials

Jason R Hattrick-Simpers¹, Zhuopeng Tan², Hiroyuki Oguchi³,
Chun Chiu¹, Edwin J Heilweil⁴, James E Maslar⁵ and
Leonid A Bendersky¹

¹ Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

² Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA

³ Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan

⁴ Physics Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

⁵ Chemicals Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

E-mail: simpers@cec.sc.edu

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Abstract

In order to increase measurement throughput, a characterization scheme has been developed that accurately measures the hydrogen storage properties of materials in quantities ranging from 10 ng to 1 g. Initial identification of promising materials is realized by rapidly screening thin-film composition spread and thickness wedge samples using normalized IR emissivity imaging. The hydrogen storage properties of promising samples are confirmed through measurements on single-composition films with high-sensitivity (resolution $<0.3 \mu\text{g}$) Sievert's-type apparatus. For selected samples, larger quantities of up to ~ 100 mg may be prepared and their (de)hydrogenation and micro-structural properties probed via parallel *in situ* Raman spectroscopy. Final confirmation of the hydrogen storage properties is obtained on ~ 1 g powder samples using a combined Raman spectroscopy/Sievert's apparatus.

Keywords: high-throughput, hydrogen storage, spectroscopy

1. Introduction

The search for hydrogen storage materials with the properties necessary for application (high gravimetric and volumetric capacities, fast kinetics, hydrogen desorption at 1 atm below 373 K, reversibility, etc) has been partially hindered by the limitations of the bulk synthesis and slow characterization techniques typically employed by the hydrogen storage community [1]. The dearth of viable materials and the extended time generally associated with screening new materials favors the application of combinatorial methodologies to help expedite the discovery of new materials. Combinatorial experiments allow one to rapidly

probe the large composition–processing–microstructure phase space required to identify and optimize new materials in a systematic manner. In conventional hydrogen storage experiments a single-composition powder is prepared by combining the precursors via chemical methods, alloying or ball milling. The hydrogen storage capabilities of the prepared material are then evaluated by volumetric/gravimetric pressure-composition isotherm (PCT) measurements in combination with *ex situ* or *in situ* structural studies, by, for example, x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy [2, 3]. Each powder can contain as many as five components, which need to be varied individually, along with the refinement of the grain size for

each composition, to identify a suitable material. In general, a long time is required to prepare a single-composition powder, typically >2 h of milling time, and to characterize a powder with a PCT Sievert's-type apparatus, typically >2 days. Combinatorial methodologies can potentially decrease the time required to screen new materials and, therefore, expedite materials discovery.

Several groups have previously developed combinatorial methodologies to identify promising hydrogen storage materials in both the bulk and thin-film forms. Groups at GE, Wildcat Discoveries and General Motors have all developed systems that can synthesize and measure the PCT characteristics of up to 48 individual powder samples simultaneously [4–6]. Common to the three systems is that the powder samples are prepared in parallel ball-milling chambers and then screened using a parallel volumetric PCT system. In the thin-film community, where quantitative measurements of the hydrogen content in combinatorial samples are not possible, most work has focused on the physical vapor deposition of composition-spread samples and primary screening of the thermodynamics and kinetics of hydrogen storage properties through measurements of secondary properties associated with hydrogenation. Rapid screening measurements for thin films have been demonstrated including measurements of film transparency, the stress of MEMS bimorphs, normalized IR emissivity (NIRE) and *ex situ* XRD studies [7–10].

Although significant efforts have been made to increase the throughput of both bulk and thin-film studies, a number of problems remain [4–10]. In the case of bulk studies the large cost associated with designing and automating the ball milling and PCT systems leads to limited sampling of composition-processing space and thus reduced throughput. Additionally, the kinetics of (de)hydrogenation and the chemical pathways leading to the dehydrogenated powder can be altered significantly by changes in the grain size, powder morphology and the order in which the precursors are mixed. These parameters can be difficult to control using ball milling. Finally PCT measurements are useful for determining the thermodynamics and kinetics of hydrogen desorption, but provide only limited information regarding the chemical/structural state of a powder during cycling. Thin-film studies can offer increased throughput by increasing the composition–processing–microstructure space that can be reproducibly addressed. However, with the exception of *ex situ* XRD studies, most thin-film screening techniques only provide indirect measurements of the presence of hydrogen in a film. Such techniques are often insensitive to multiple phase transformations and the formation of new phases, which are common during the cycling of hydrogen storage materials.

Furthermore, we are unaware of any work that has attempted to systematically bridge the gap between the characterization of thin-film and bulk powder material forms. This would require devising a comprehensive scheme capable of measuring samples with masses spanning several orders of magnitude. Such a scheme could take advantage of the increased throughput of thin-film combinatorial libraries by using indirect characterization techniques for primary

screening. Compositions and microstructures identified as promising would need to be confirmed in thin-film form via quantitative hydrogenation measurements. Larger quantities of the most promising samples, e.g. masses up to ~100 mg, could be utilized for secondary screening via a parallel characterization technique. Extensive PCT single-powder measurements can be performed for final verification.

Here we present a comprehensive high-throughput measurement protocol, involving a suite of measurement techniques, which can determine the hydrogen storage properties of materials with masses spanning nine orders of magnitude. Initial screening of the kinetic and thermodynamic properties can be accomplished through NIRE imaging studies of thickness wedge samples and composition-spread samples, respectively. Promising compositions can be verified by PCT/kinetic measurements of a single-composition thin film using a high-sensitivity Sievert's-type apparatus. For the most promising materials, powder samples can be synthesized so that the hydrogenation properties, chemical pathways and cycling properties can be characterized using a parallel *in situ* Raman spectroscopic measurement system. Final characterization of hydrogen storage characteristics is performed with a Raman spectroscopy/PCT Sievert's-type setup that provides information on the chemical state of the material as well as a quantified measure of the thermodynamics, kinetics and the mass fraction of hydrogen stored in the powder.

2. Experimental details

All thin-film samples in this study were deposited in an ultra-high vacuum electron beam evaporation system (base pressure $\sim 10^{-8}$ Torr) with two electron beam sources each containing six different pockets. Composition spread and wedge samples were all deposited using a shadow masking system as described in detail in [11]. Prior to removal from the deposition chamber, all samples were capped with 6–10 nm of Pd to prevent oxidation. All mixed powder samples were formed by high-energy ball milling of commercially available precursor powders. Prior to measurement the powders and thin films were stored inside an Ar filled glove box with a water concentration of less than 1×10^{-7} mol H₂O mol⁻¹ Ar (0.05×10^{-6}). The thin films were briefly exposed to air during their transfer from the deposition chamber to the glove box, and then again during transfer to the NIRE or PCT system. All powder preparation, handling, and loading was carried out inside the glove box and the powders were always transported in a protective environment.

The NIRE system used here has been described in detail in a previous publication [12]. Briefly, the films were measured in a specially designed hydrogenation chamber fitted with a sapphire window. The window permits direct optical imaging of the sample surface with an IR camera via a CaF₂ lens. The samples were mounted onto a substrate heater and the IR emissivity of each film was monitored as a function of pressure, temperature and time.

A custom-developed PCT Sievert's-type apparatus was used for both powder and thin-film samples and will

be described in detail elsewhere. The sample cell has a total volume of 10 cm^3 and an optical window, which allows for simultaneous PCT/Raman spectroscopic or NIRE measurements of powders or thin films. By combining the relatively small sample cell volume with a high-sensitivity pressure transducer, the hydrogenation of single films as thin as 100 nm can be accurately measured.

Raman spectroscopic measurements were performed in a backscattering geometry using 514.5 nm radiation from an argon ion laser. Laser radiation with a power of approximately 50 mW was focused onto the powder with a spherical lens of 300 mm focal length. The scattered radiation was collected and collimated with an $f/4$ achromatic lens located at an infinite conjugate ratio. A detailed description of the Raman spectroscopic measurement system can be found in [13]. All spectra were obtained within an integration time of 6 s or less. The Raman spectral positions were determined by fitting the respective spectral peaks at each temperature with Lorentzian line shapes.

3. Results and discussion

3.1. NIRE measurements of composition-spread samples

The principle of NIRE measurements of hydrogen storage materials relies on the fact that during the absorption of hydrogen many materials undergo a metal-insulator transition that increases the IR emissivity and transparency of the film. The spectral range of these changes can be broad, but most materials exhibit changes between 0.1 and $5.5\text{ }\mu\text{m}$, which is within the detection range of the camera used in these studies. One approach is to measure changes in the intrinsic IR emissivity of a material resulting from changes in the hydrogen content (either due to solubility or the formation of hydrides). In another approach, the increase in the optical transparency of the hydrogenated film, particularly in the IR region, allows IR radiation from a selected heated substrate to be transmitted through the film and detected by an IR camera. Either approach provides a qualitative measure of how much of the film has transformed to the hydride phase as a function of temperature, pressure and time. Two types of experiments will be discussed here. In the first type, measurements on composition-spread samples are performed and the relative effect of composition on the pressure and temperature of hydrogen absorption/desorption is monitored. In the second type, measurements on thickness wedge samples held at a constant pressure and temperature provide detailed information about the effect of promising additives on the kinetics of hydrogenation.

As an example of measurements on a composition-spread sample, NIRE imaging has been used to provide insight into the effect of transition metal (TM) additives such as Fe, Ti and Ni on the thermodynamics and kinetics of hydrogenation in Mg thin films. Here binary composition spreads of the form $\text{Mg}_{1-x}\text{TM}_x$ were deposited on sapphire substrates and cycled at different temperatures and hydrogen pressures. The images obtained from the IR camera were then processed with in-house developed software, the IR intensity of the

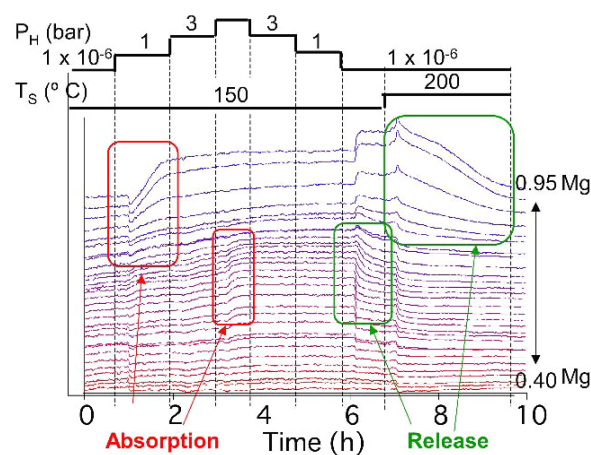


Figure 1. NIRE mapping of a $\text{Mg}_{1-x}\text{Ni}_x$ composition spread sample as a function of pressure and temperature. Changes to the thermodynamics of hydrogen absorption/release can be extracted by monitoring the pressure and temperature at which NIRE increases/decreases; for instance, for Mg compositions >0.3 an increase in the NIRE signal is observed at a hydrogen pressure of 5 bars.

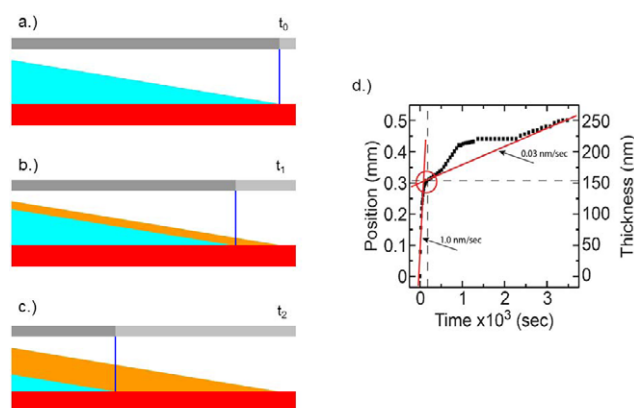


Figure 2. NIRE mapping of a Mg–Ti wedge sample as a function of time. (a) Schematic of as-deposited film (blue wedge), substrate (red), hydride surface layer (orange) and NIRE image of wedge and exposed substrate. (b, c) Schematic after exposure to hydrogen for two different times, showing the movement of the light region in the NIRE image as the hydride layer thickens. (d) Plot of the hydride growth rate.

samples was normalized by the intensity of a hydrogen-inert reference material, and then the IR intensity was summarized along with the history of the film as shown in figure 1. These figures provide an estimation of the pressures and the rates at which hydrogen is absorbed/desorbed as a function of composition and temperature. One can see, for instance, that as the Ni content is increased to $x \approx 0.3$, the pressure required for the initial hydrogenation of the films increases from less than 1 bar to greater than 3 bars, and the film begins to release hydrogen at lower temperatures, possibly indicating the formation of the complex hydride Mg_2NiH_4 [9].

For quantitative information on the kinetics of hydrogenation of interesting samples, single-composition wedge samples were deposited as schematically illustrated in figure 2(a). Prior to exposure to hydrogen, only the portion of the substrate that had not been coated with the

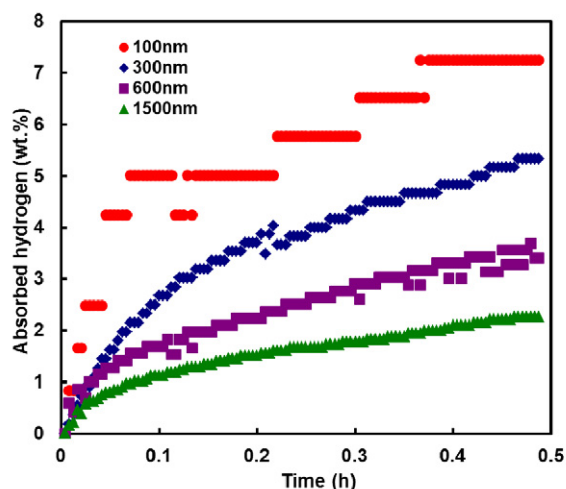


Figure 3. A series of kinetic hydrogenation measurements on Mg thin films with various thicknesses (from 100 to 1500 nm) at 423 K in 0.1 MPa hydrogen, demonstrating the resolution of the Sievert's apparatus.

film showed significant emission. Shortly after exposure to hydrogen, the thinnest portion of the film transformed to the transparent hydride, permitting the passage of the strong IR radiation from the substrate up to the blue line shown in figures 2(b) and (c). As the hydride phase continued, to grow the bright region of the IR image moved, because the boundary between the light and dark areas is directly correlated to the completely hydrogenated thickness of the film. By monitoring the boundary between the two regions as a function of time, and assuming that the hydride phase grows as a continuous layer, the hydride growth rate can be calculated, as shown in figure 2(d). From this method, a quantitative understanding of the effect of additives on the kinetics of hydrogenation can be obtained. Additionally, since many hydrides of interest exist as powders, core-shell particles with the hydride acting as a hydrogen-impermeable shell are formed. The hydride shell limits the diffusion rate during loading; hence, wedge measurements can provide useful information regarding optimal grain sizes for rapid kinetic cycling [14].

3.2. Single-film volumetric PCT measurements

Once a 'hit' has been identified through NIRE measurements of composition spread or wedge thin-film samples, it is important to verify the results through a direct measurement of the hydrogen content. To this end, we have developed a high-sensitivity Sievert's-type apparatus capable of monitoring changes in the hydrogen content of a single 100 nm \times 1 cm² film. Figure 3 shows kinetic data for pure Mg thin films ranging in thickness from 100 to 1500 nm, here the ultimate resolution of the Sievert's-type apparatus can be observed to be $<0.3 \mu\text{g}$. The ability to measure the hydrogen content in a thin film allows one to evaluate the enthalpy of reaction, the activation energy, $T_{1\text{ bar}}$, and hydrogen cycling properties of a thin film. This provides a final check for false positives in candidate thin films prior to the synthesis via bulk methods.

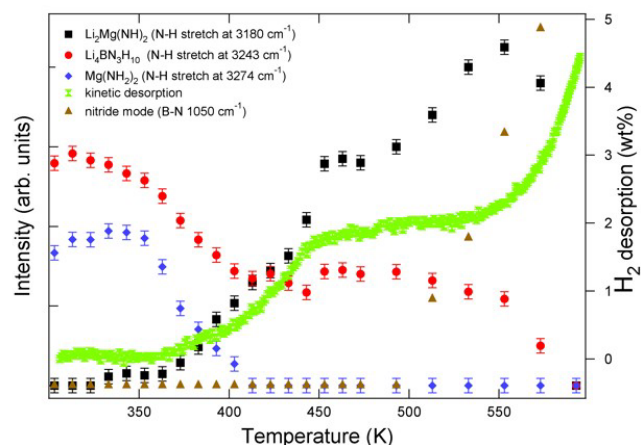


Figure 4. Normalized Raman intensities (left axis) of the initial phases, $\text{Li}_4\text{BN}_3\text{H}_{10}$, (red circles), $\text{Mg}(\text{NH}_2)_2$ (blue diamonds) and the product phases, $\text{Li}_2\text{Mg}(\text{NH})_2$, (black squares) and an unindexed nitride phase (brown triangles) are plotted as a function of temperature. The desorbed hydrogen (green crosses) as measured by a Sievert's-type apparatus is plotted on the right axis. Through this measurement technique, chemical reactions occurring in the powder can be observed and correlated with hydrogen evolution.

3.3. High-throughput Raman spectroscopy

Thin films often exhibit properties (i.e. kinetics and thermodynamics) that deviate from those of bulk behavior owing to factors such as epitaxial stress, stresses due to the substrate clamping and metastable/unstable phases formed during deposition. It is therefore imperative to validate all thin-film results via bulk methods. Although multiple-reactor Sievert's-type apparatuses provide quantitative information about the thermodynamics, kinetics and mass fraction of hydrogen desorbed by a powder, they require extensive piping and valving and are therefore expensive to manufacture. An alternative primary powder-screening technique is preferred that reduces cost and increases throughput while providing additional structural information that is useful for identifying the materials present during hydrogen cycling. Vibrational spectroscopic measurements of complex hydride materials are frequently reported owing to their sensitivity to hydrogen's chemical bonds and the overall structure of the hydride. We have recently reported that *in situ* Raman spectroscopy can be used to probe the pressure-temperature properties of mixed complex hydrides during hydrogen cycling [13]. We have designed a high-throughput optical cell enabling the *in situ* Raman measurement of up to 18 individual powders at a hydrogen pressure of up to 10 MPa and temperature of up to 873 K. The cell is compatible with either serial measurements via translation of the optical cell or imaging measurements.

An example of the utility of Raman spectroscopy in the study of hydrogen storage materials can be obtained from a comparison of the Raman spectra of $\text{Li}_4\text{BN}_3\text{H}_{10}$ – $\text{Mg}(\text{NH}_2)_2$ – MgH_2 and its kinetic desorption curve (taken in a separate measurement), as shown in figure 4. Figure 4 reveals that the initial powder contains a mixture of $\text{Li}_4\text{BN}_3\text{H}_{10}$ and $\text{Mg}(\text{NH}_2)_2$, which begin to decompose to evolve hydrogen and form a secondary phase $\text{Li}_2\text{Mg}(\text{NH})_2$ at about 353 K. One can infer that at this temperatures the

$\text{Li}_4\text{BN}_3\text{H}_{10}$ and $\text{Mg}(\text{NH}_2)_2$ react with the residual MgH_2 , from its presence according to the results of XRD studies of the as-prepared powder and the formation of $\text{Li}_2\text{Mg}(\text{NH})_2$ as a byproduct, although the direct reaction of the two cannot be discounted. The hydrogen evolution and reactions continue to 450 K, where kinetic limitations are most likely preventing the complete reaction of the $\text{Li}_4\text{BN}_3\text{H}_{10}$ at the ramp rate used (10 K min^{-1}). Above 500 K there is a second evolution of hydrogen in conjunction with the further decomposition of the remaining $\text{Li}_4\text{BN}_3\text{H}_{10}$. However, during this decomposition, a nitride phase is formed in addition to $\text{Li}_2\text{Mg}(\text{NH})_2$. It is well established that nitride phases are difficult to fully rehydrogenate under mild conditions; thus, the formation of the nitride phase at temperatures greater than 500 K represents an upper bound on the temperature that the powder can be exposed to. Subsequent *in situ* rehydrogenation experiments can give insights into the reversibility of a powder is, particularly if the original phases are reformed, if new hydride phases are formed, or if a significant fraction of the powder remains in the form of a byproduct phase (i.e. nitride). This represents one advantage of using high-throughput Raman spectroscopy over traditional volumetric/gravimetric measurements since it can provide insight into not only the desorption temperature and kinetics of each powder but also into the chemical reactions taking place during cycling, the presence of deleterious phases, and their role in the reversibility of the powder. Thus one can rapidly screen powders for the pressure-temperature-time envelope in which they can be reproducibly used.

3.4. Combined volumetric/Raman spectroscopic system

Once a promising material has been identified via thin-film composition spreads, verified by high-sensitivity volumetric measurements, scaled up to mg quantities and tested in parallel with other promising compositions by high-throughput Raman spectroscopy, a final in-depth volumetric measurement of the powder in gram quantities is necessary for final verification of its hydrogen storage properties. During the final verification, it is also important to monitor the structural/chemical state of the powder as a guide to future experiments. To this end we have developed an optical cell that allows for combined volumetric and Raman spectroscopic measurements of gram quantities of powders. The system will be described in more detail in a future publication; it utilizes the same custom-made high-sensitivity system described earlier for the Sievert's-type apparatus but is modified to include a sapphire window for optical access to the powder. The optical cell is capable of reaching pressures of as high as 6 MPa and temperatures of up to 773 K. Using this cell, quantitative data on the thermodynamics, kinetics and the amount of hydrogen that can be reversibly stored in the powder can be mapped in combination with the phase content during cycling.

Figure 5 shows example data from a simultaneous volumetric/Raman spectroscopic measurement on a $\text{Li}_4\text{BN}_3\text{H}_{10}$ - $\text{Mg}(\text{NH}_2)_2$ - MgH_2 powder. A comparison of figures 4 and 5 demonstrates that hydrogen desorption does indeed begin at the same time as the decomposition of

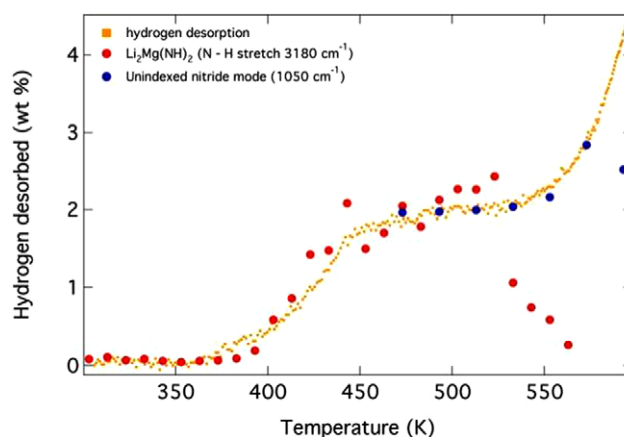


Figure 5. Example of combined Sievert's PCT and Raman spectroscopic measurements, illustrating that the relative proportion of the product phase present is correlated with the amount of evolved hydrogen. Here the normalized Raman intensities of the product phases formed during hydrogen desorption $\text{Li}_2\text{Mg}(\text{NH})_2$ (red circles) and an unindexed nitride phase (blue circles), are compared with the wt% hydrogen (orange squares) desorbed during temperature ramping.

both initial phases, moreover it shows that the second kinetic desorption is indeed accompanied by the formation of an irreversible nitride phase. This final check of the reversible hydrogen content of the powder is vital, as not all the product phases may be Raman active, or they may exhibit low scattering cross sections. Thus, a Raman inactive or weakly scattering parasitic phase could form in low concentrations after each cycle, slowly degrading the overall mass fraction of hydrogen that can be stored in the powder.

4. Conclusions

A high-throughput characterization scheme has been demonstrated that accurately measures the hydrogen storage properties of materials in quantities ranging from $\sim 10\text{ ng}$ to 1 g. The initial identification of promising materials is realized by rapidly screening thin-film composition spread samples using NIRE imaging. The hydrogen storage properties of promising samples are confirmed through measurements on single-composition films with a high sensitivity (resolution $<0.3\text{ }\mu\text{g}$) Sievert's-type PCT apparatus. A selection of samples can then be scaled up to $\sim 100\text{ mg}$ powder samples and then their (de)hydrogenation/micro-structural properties are probed via parallel *in situ* Raman spectroscopy. Final confirmation of the hydrogen storage properties is obtained for $\sim 1\text{ g}$ powder samples utilizing a combination of Raman spectroscopy and Sievert's PCT measurements.

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